THE ISOTOPIC COMPOSITION OF MOLYBDENUM IN SINGLE PRESOLAR SILICON CARBIDE GRAINS

; G. K. Nicolussi[1,2], A. M. Davis[1], M. J. Pellin[2], R. S. Lewis[1], R. N. Clayton[1,3,4] and S. Amari[1,5], [1]Enrico Fermi Inst., [3]Dept. of Chemistry, [4]Dept. of the Geophysical Sciences, The University of Chicago, Chicago, IL 60637; [2]Chemistry and Material Science Divisions, Argonne National Laboratory, Argonne, IL 60439; [5]Present address: McDonnell Center for Space Sciences, Washington University, St. Louis, MO 63130.

Abstract. We report the isotopic composition of molybdenum in three mainstream presolar SiC grains from Murchison. Normalized to terrestrial Mo isotopic compostion and to the pure *s*-process isotope ^{96}Mo, all three grains are strongly depleted in *p*-process ^{92}Mo and ^{94}Mo, *r*- and *s*-process ^{95}Mo, ^{97}Mo, and ^{98}Mo and *r*-process ^{100}Mo. The largest depletions are in the pure *p*- and *r*-process isotopes, as expected from *s*-process nucleosynthesis in AGB stars.

Introduction. Measurements of the isotopic compositions of Kr, Xe, Sr, Ba, and Nd in aggregates of SiC grains from the Murchison meteorite have shown strong enhancements in the isotopes produced by *s*-process nucleosynthesis [1]. We have developed a new technique for isotopic analysis of individual presolar grains and used it to show that Murchison SiC grains are strongly depleted in *r*-process ^{96}Zr relative to the other Zr isotopes, all of which are produced by the *s*-process [2]. We have recently added the capability of Mo isotopic analysis and have applied it to SiC grains.

Mo is a particularly interesting element, because it has two *p*-process isotopes, ^{92}Mo and ^{94}Mo, that are shielded from both the *s*- and *r*-processes, a pure *s*-process isotope, ^{96}Mo, that is shielded from the *r*-process and a pure *r*-process isotope, ^{100}Mo, which cannot be produced by the *s*-process because of the short half-life of ^{99}Mo. The remaining stable isotopes, ^{95}Mo, ^{97}Mo and ^{98}Mo can be produced by the *r*- or *s*-processes. Mo also has the advantage that all of its isotopes are relatively abundant: the rarest isotope, ^{94}Mo comprises ~9% of terrestrial Mo. Mo has not been reported in the literature to be present in presolar SiC grains, although both Mo and Zr occur as carbide inclusions in presolar graphite [3]. We report here that not only is Mo present in presolar SiC, it is isotopically highly anomalous.

Experimental. Isobaric interferences from other elements that occur in presolar SiC have the potential to cause considerable difficulty in Mo isotopic analysis. Mo has seven stable isotopes, 92, 94, 95, 96, 97, 98, and 100 and has isobaric overlaps with Zr at masses 92, 94, and 96, Ru at masses 96, 98, and 100, and Ti$_2^+$ at all Mo masses. Zr and Ti are known to be present in SiC grains and Ru is present in SiC grain-size aggregates. The mass resolution needed to resolve these interferences, M/ M of 3×10^4 to 10^6, is beyond the capability of currently available secondary ion mass spectrometry (SIMS) instruments. We have developed a new

instrument, CHARISMA [2,4,5], that gets around this difficulty by resonantly ionizing ablated Mo atoms while leaving Zr and Ru atoms and Ti$_2$ molecules in the neutral state. For low desorption laser intensities at the sample surface (10^8–10^9 W cm^{-2}), the majority of secondary particles consists of neutral atoms. As a result, secondary neutral mass spectrometry (SNMS) has a potentially higher useful yield than SIMS. For the analysis of one element, resonant ionization mass spectrometry (RIMS) is an excellent method to mass analyze neutral atoms in a specific electronic state. RIMS has demonstrated high selectivity as well as high sensitivity.

CHARISMA is equipped with an all-reflecting Schwarzschild-type optical microscope, in which spherical mirrors are arranged in a way that superficially resembles a Cassegrain telescope. This microscope allows the sample to be viewed with ~0.5 μm resolution and permits introduction of a laser for ablation of the sample. The instrument is operated in a pulsed mode at 60 Hz; each pulse consists of the following sequence: (1) a ablation laser pulse, focused on a SiC grain or standard, produces a cloud of neutral atoms, ions and molecules; (2) a voltage pulse is applied to the sample to electrostatically suppress the ions; (3) beams from two XeCl excimer-pumped dye lasers intersect the cloud of neutral species above the sample, resonantly ionizing Mo with high efficiency and nonresonantly ionizing other species with low efficiency; (4) a high voltage pulse extracts and accelerates the ions; (5) the ions are mass-analyzed in a time-of-flight mass spectrometer.

Desorption of our samples was achieved with pulsed 355 nm laser radiation (pulse length ~10 ns) which was generated by frequency tripling the fundamental wavelength of a diode-pumped Nd:YAG laser (1064 nm). In order to control the desorption yield from the target surface, the laser light was attenuated with a variable neutral density filter that allows precise control of the incident laser energy.

In order to postionize laser desorbed neutral Mo atoms from presolar SiC grains, we have chosen a two-color resonant ionization scheme. The resonant laser radiation was generated by two tunable dye lasers which were pumped by a pulsed XeCl excimer laser (20 ns pulse length). The output of one dye laser was frequency doubled in a KDP-C crystal producing 313.26 nm laser radiation. This radiation excites Mo atoms resonantly from the a^{7}S$_3$ ground state to the intermedi-

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ate $y^7P^o_4$ state. The second dye laser was tuned to a wavelength of 388.2 nm which ionizes the excited Mo atoms by a resonant transition into an autoionization state just above the ionization limit. The laser intensity of the 388.2 nm radiation reaching the target region was approximately 10^7 W cm^{-2}; the resonant excitation was found to saturate easily and its laser intensity was kept below 10^5 W cm^{-2}. This ionization scheme provides excellent discrimination against nonresonant ionization of Zr, which is the most likely isobaric interference.

Results and discussion. We found detectable levels of Mo in three SiC grains from the mount of grain-size separate KJH, which is described in our companion abstract [2]. The Mo isotopic compositions of these grains are shown in Fig. 1. Normalized to terrestrial composition and to *s*-process-only ^{96}Mo, all three grains are depleted in all other isotopes by several hundred permil. The largest depletions are in the *p*-process isotopes ^{92}Mo and ^{94}Mo and the *r*-process isotope ^{100}Mo, because not only does the *s*-process produce ^{95}Mo, ^{96}Mo, ^{97}Mo, and ^{98}Mo, it burns ^{92}Mo, ^{94}Mo, and ^{100}Mo by neutron capture. Interestingly, grain 154, the only grain for which both Mo and Zr isotopes were measured, is depleted in ^{96}Zr (*r*-process only) [2] by about the same amount as it is in ^{92}Mo, ^{94}Mo, and ^{100}Mo. ^{95}Mo, ^{97}Mo, and ^{98}Mo are also depleted relative to ^{96}Mo, reflecting the *r*-process contribution to these isotopes in the normalizing terrestrial Mo isotopic composition. Also shown in Fig. 1 are evolutionary tracks for successive third dredge-up episodes for a 3 solar mass AGB star with twice the solar metallicity [6]. The primary neutron source for the *s*-process is ^{13}C(,n)^{16}O. ^{13}C is produced when hydrogen diffuses below hydrogen-rich envelope during third dredge-up, producing a ^{13}C pocket. The ^{13}C burns during the interpulse period and causes *s*-process nucleosynthesis [7]. During the next third dredge-up, newly synthesized *s*-process material is mixed into the envelope. The size of the ^{13}C pocket in these calculations is arbitrary and was chosen to provide the best match with the light element isotopic compositions of mainstream SiC grains [6]; other calculations with different ^{13}C pocket amounts and with 1.5 solar masses give quite similar trajectories. SiC grains must have condensed around stars from material ejected from the convective envelope. The trajectories on Fig. 1 start with solar isotopic composition and reflect mixing in of increasing amounts of *s*-process nucleosynthesis products. The C/O ratio of the envelope increases with successive third dredge-up episodes. On Fig. 1, the symbols change from ×s to circles when the C/O ratio exceeds 1 and SiC (rather than silicates) can condense.

The excellent agreement between the measured Mo isotopic composition of three presolar grains and the

calculations indicates not only that the neutron capture cross sections in the AGB evolutionary code are about right, but also that the assumption of an approximately solar initial isotopic composition for AGB stars is justified. In particular, there is no significant variation in the proportions of *r*- and *p*-process isotopes in the three grains. Finally, measurements on nearly pure *s*-process Mo, such as in the most extremely fractionated grain in Fig.1, should allow more accurate assessment of the *r*-process contribution to solar system Mo.

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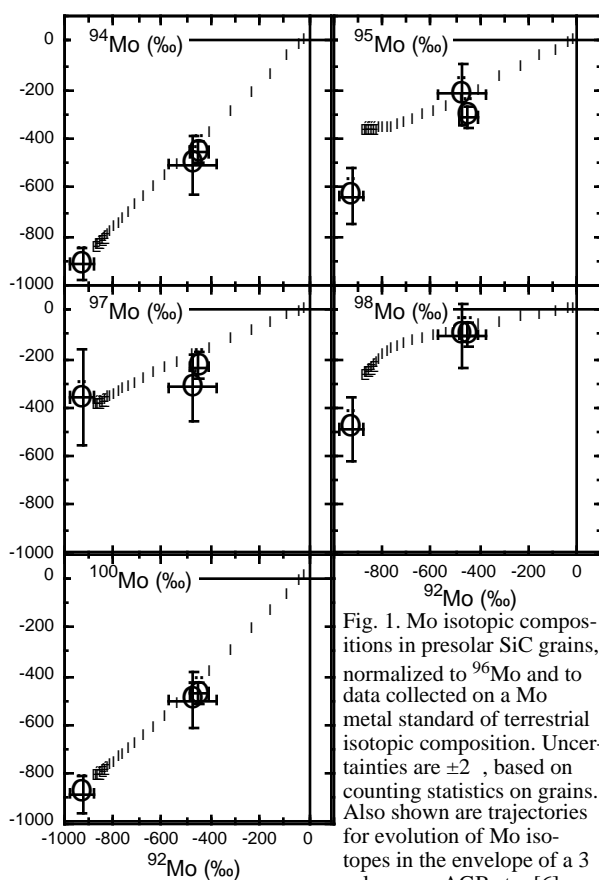

Fig. 1. Mo isotopic compositions in presolar SiC grains, normalized to ^{96}Mo and to data collected on a Mo metal standard of terrestrial isotopic composition. Uncertainties are ±2 , based on counting statistics on grains. Also shown are trajectories for evolution of Mo isotopes in the envelope of a 3 solar mass AGB star [6].